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New numerical model for thermal quenching mechanism in quartz based on two-stage thermal stimulation of thermoluminescence model

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Abstract The effect of thermal quenching plays an important role in the thermoluminescence (TL) of quartz on which many applications of TL are based. The studies of the stability and kinetics of the 325 °C thermoluminescence peak in quartz are described by Wintle (1975), which show the occurrence of thermal quenching, the decrease in luminescence efficiency with rise in temperature. The thermal quenching of thermoluminescence in quartz was studied experimentally by several authors. The simulations work presented in the literature is based on the single-stage thermal stimulation model of thermoluminescence, in spite of that the mechanisms of this effect remain incomplete. This paper presents a new numerical model for thermal quenching in quartz, using the previously published two-stage thermal stimulation of thermoluminescence model.

1. Introduction

The thermal quenching of luminescence efficiency is an effect which is present in many thermoluminescent (TL) materials. It causes a significant decrease of the luminescence signal and disturbs the shape of the glow-peaks. Among the TL materials which exhibit thermal quenching, the most widely known and investigated are Al_2O_3:C (Akselrod et al., 1990, 1998; Kitis et al., 1994) and Quartz (Wintle, 1975; McKeever et al., 1997; Kitis et al., 2003; Petrov and Bailiff, 1996, 1997; Chitambo, 2003). Heating rate is one of the most important experimental variables, which changes the glow curve shape (Ogundare et al., 2005). In TL dosimetry, the absorbed dose and TL intensity are affected by changes in the heating rate (Betts et al., 1993; Taylor and Lilley, 1982).

Many investigations have been carried out by scientists in order to understand that how the TL glow curve changes under different heating rates (Taylor and Lilley, 1982; Nakajima,

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1976; Jain, 1978; Spooner and Franklin, 2002). The decrease of luminescence efficiency with temperature increase due to the increased probability of non-radiative transitions is known as thermal quenching (Curie, 1963).

The effect of thermal quenching may be observed while performing a series of TL measurements with different heating rates. Typically, with increasing heating rate, the maximum of a TL glow peak shifts to higher temperatures. At a higher temperature, the luminescence is quenched more intensely so that the whole area under TL peak decreases.

The thermal quenching efficiency versus temperature, $\eta(T)$, is given by the following equation (Petrov and Bailiff, 1996, 1997):

$$\eta(T) = \frac{1}{1 + C.\exp(-\frac{W}{kT})}, \tag{1}$$

where C and W are 'quenching parameters'. T is the sample temperature and k is the Boltzmann constant (Akselrod and Larsen, 1998).

(Wintle, 1975), measured the thermal quenching parameters of annealed natural quartz using radioluminescence as $C = 2.8 \times 10^7$ and $W = 0.64$ eV indicating that the quenching properties are independent of the wavelength of the observed luminescence, except at 495 nm. In this study the thermal quenching parameter values of (Wintle, 1975) will be considered as reference values. As a result of many studies, a decrease in TL intensity was observed with an increase in the heating rate. This phenomenon has been explained to be due to thermal quenching, whose efficiency increases as temperature increases (Spooner and Franklin, 2002).

The thermal quenching mechanism in quartz based on time-resolved optically stimulated luminescence has been studied by Pagonis et al. (2010). The aim of the present paper is to investigate a new numerical model which described a thermal quenching in quartz, based on the previously suggested two-stage thermal stimulation of thermoluminescence model by Chen et al. (2012).

2. The proposed model

Fig. 1 shows the energy level diagram of the proposed model based on the two-stage thermal stimulation of thermoluminescence mechanism (Chen et al., 2012). The model consists of many trapping states and one kind of recombination center, with the corresponding electronic transitions taking place during excitation and heating stages.

In the model described below, N(cm^{-3}) is the concentration of the trapping state, n_1(cm^{-3}) is their instantaneous occupancy; n_e(cm^{-3}) is the instantaneous occupancy of the excited state. The activation energy and the frequency factor for this transition are E_1(eV) and s_1(s^{-1}), respectively. Once the electron is in the excited state, it can either retrap with a probability of p(s^{-1}) or be thermally excited into the conduction band. The activation energy and the frequency factor for this transition are E_2(eV) and s_2(s^{-1}), respectively. n_c(cm^{-3}) are the instantaneous concentration of electrons in the conduction band. A_n(cm^3 s^{-1}) is the retrapping probability coefficient of electrons from conduction band into the excited state, A_m(cm^3 s^{-1}) is the recombination probability of electrons with holes in the recombination centers.

The electronic transition from the conduction band into the excited state of recombination center (located below the conduction band) is denoted by the probability A_{n2}. The direct radiative transition from the excited level into the ground electronic state of recombination center is given by the probability A_m, this recombination is assumed to produce the TL photons with an instantaneous intensity I. The probability for the competing thermally assisted process is given by a Boltzmann factor of the form $A_{\mathrm{NR}}.\exp(-W/k_BT)$ where W represents the activation energy for this process and A_{NR} a constant representing the non-radiative transition probability coefficients (s^{-1}). The dashed arrow denotes the non- radiative process into the ground state, N_2(cm^{-3}) and n_2(cm^{-3}) are the concentrations of electron traps and filled traps correspondingly in the excited state of the recombination center, M(cm^{-3}) and m(cm^{-3}) are, respectively the concentration of traps and holes in the ground electronic state of recombination center.

The simultaneous differential equations governing the process during the heating stage, shown in Fig. 1 are:

$$\frac{dn_1}{dt} = -s_1 n_1 \exp(-E_1/kT) + p n_e, \tag{2}$$

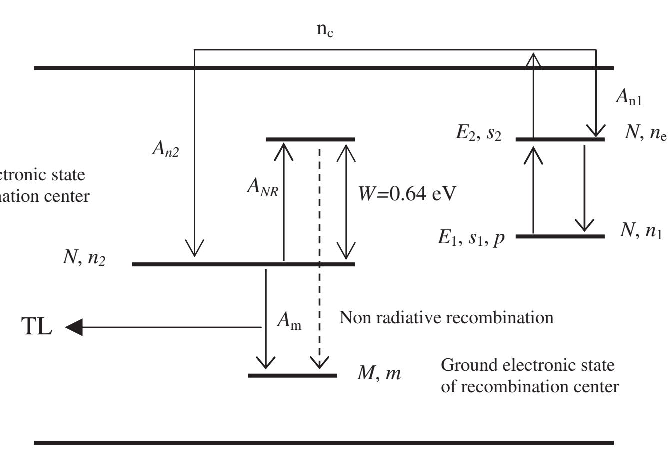

Figure 1 Schematic diagram of the thermal quenching model for quartz, using the two-stage thermal stimulation of the thermoluminescence model. The various transitions shown and the parameters used in the model are described in the text.

$$\frac{dn_e}{dt} = A_{n1}(N - n_1 - n_e)n_c + s_1 n_1 \exp(-E_1/kT) - s_2 n_e \times \exp(-E_2/kT) - pn_e, \quad (3)$$

$$\frac{dn_2}{dt} = A_{n2}n_c(N_2 - n_2) - A_m n_2 - n_2 A_{NR} \exp(-W/kT), \quad (4)$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn_1}{dt} - \frac{dn_e}{dt} - \frac{dn_2}{dt}. \quad (5)$$

The emitted light is taken to be proportional to the rate of recombination so that:

$$I = -\frac{dm}{dt} = A_m n_2 \eta(T), \quad (6)$$

where η is the luminescence efficiency, K is a dimensionless constant 2.8×10^7 and W is an activation energy, $W = 0.64$ eV (Wintle, 1975).

3. Results and discussions

In the present study, the numerical solution was performed using the MATLAB ode15s program. This program was used to solve numerically the relevant sets of Eqs. (2)–(6), for appropriately chosen sets of trapping parameters. An important result of the model is that it reproduces the well-known decrease in the thermoluminescence (TL) signal due to thermal quenching. Specifically when TL glow curves are measured using different heating rate values (from 5 to 20 K/s), with increasing heating rate the glow peaks shift toward higher temperature and the TL intensity reduces, which may be due to the well known phenomena of thermal quenching of TL due to increase in heating rates. It is a goal point that the physical model does not need to resort to the quasi-equilibrium approximation. The thermal quenching phenomena can be also explained by the enhancement of the non radiative recombination in the forbidden band of this material. A second important point of the presented model is that it reproduces the thermoluminescence (TL) glow peak at 598 K of quartz (Wintle, 1975). The result of simulating the TL glow curves using the set of trapping parameters given in the caption is shown in Fig. 2.

4. Method of analysis

(Randall and Wilkins, 1945a,b) provided the simplest mathematical representation for the luminescence glow peaks without any overlapping. The basic assumptions they made were that once an electron escapes from a trap there is no significant probability for it to get retrapped and that the luminescence intensity at any temperature is directly proportional to rate at which the detrapping occurs. During heating, if n is the concentration of filled traps at any time t (temperature $= T$) then the intensity of TL is given by:

$$I(t) = -\frac{dn}{dt} = sn \exp\left\{-\frac{E}{kT}\right\}. \quad (7)$$

This differential equation describes the charge transport in the lattice as a first-order process. If the temperature is kept constant, $p = s\exp(E/kT)$ is constant and the intensity can be found from Eq. (7) by integration:

$$I(t) = I_0 \exp(-tp), \quad (8)$$

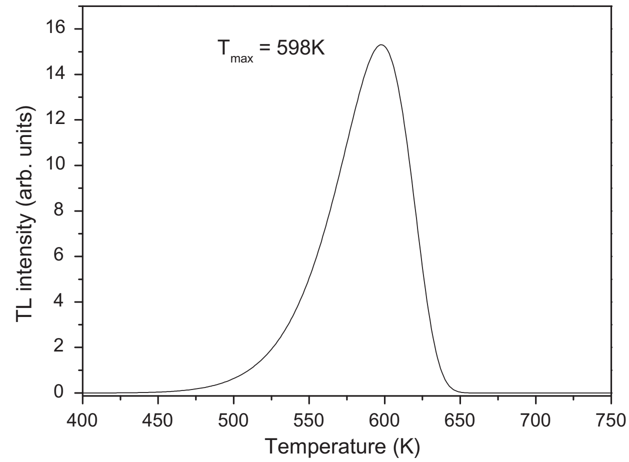

Figure 2 Simulated results of a TL peak. The parameters used were $E_1 = 1.0$ eV; $E_2 = 0.6$ eV; $p = s_1 = 10^{11}\ \mathrm{s}^{-1}$; $s_2 = 10^{12}\ \mathrm{s}^{-1}$; $A_{n1} = 10^{-12}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$; $A_{n2} = 10^{-8}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$; $A_m = 2.38 \times 10^4\ \mathrm{s}^{-1}$; $A_{NR} = 10^{-7}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$; $N = 1.1 \times 10^{10}\ \mathrm{cm}^{-3}$; $N_2 = 1.1 \times 10^{10}\ \mathrm{cm}^{-3}$; $W = 0.64$ eV; $K = 2.8 \times 10^7$; the heating rate was $\beta = 1\ \mathrm{Ks}^{-1}$.

where I_0 is the initial intensity at time $t = 0$. At a constant temperature the decay is thus a simple exponential function of time. The phenomenon is called phosphorescence. But if the temperature varies in time p is no longer a constant and the solution of the differential Eq. (7) becomes:

$$I(t) = -\frac{dn}{dt} = n_0 s \times \exp\left\{-\frac{E}{kT(t)}\right\}.\exp\left\{-s\int_0^t \exp\left\{-\frac{E}{kT(t\prime)}\right\}dt\prime\right\}, \quad (9)$$

where n_0 is the total number of trapped electrons at time $t = 0$. As the temperature increases, the intensity initially increases (detrapping of the trapped charge carriers and recombination takes place which initiates luminescence), then reaches a maximum and finally decreases (as the number of charges carriers becomes depleted). The intensity has thus the shape of a peak and (if derived from Eq. (7)) is called a first-order glow peak. Usually TL is observed as the temperature is raised as a linear function of time according to:

$$T(t) = T_0 + \beta t \quad (10)$$

with β the constant heating rate and T_0 the temperature at time $t = 0$. This gives for the intensity as function of temperature

$$I(t) = -\frac{1}{\beta}\frac{dn}{dt} = n_0 \frac{s}{\beta} \times \exp\left\{-\frac{E}{kT}\right\}.\exp\left\{-\frac{s}{\beta}\int_{T_0}^{T} \exp\left\{-\frac{E}{kT\prime}\right\}dT\prime\right\}, \quad (11)$$

Eq. (11) is the well-known Randall–Wilkins first-order expression of a single glow peak. The peak has a characteristic asymmetric shape being wider on the low temperature side than on the high temperature side.

The peak 598 K shown looks like a simple first-order peak, with a geometrical factor of $\mu = 0.41$. The peak-shape method (Chen, 1969) has been used for evaluating the activation energy; this energy is given by the following expression:

$$E_\omega = kT_m\left(2.52\frac{T_m}{\omega} - 2\right). \tag{12}$$

The frequency factor is defined by:

$$s = \frac{\beta E}{kT_m^2}\exp(E/kT_m). \tag{13}$$

From the simulated result presented in Fig. 2, we get $E_\omega = 1.2$ eV and $s = 1.06 \times 10^{10}\ s^{-1}$.

5. The luminescence efficiency

The luminescence efficiency is generally a temperature sensitive factor, efficiency decreasing with increase of temperature. This is so because of a competition between radiative transitions (which are almost temperature-independent) and non-radiative transitions – de-excitation of material by thermal agitation – which increases with temperature. In the case of a TL phosphor having one kind of luminescence centre and several thermal activation energies, this will mean that the higher temperature peaks are observed under decreased luminescence efficiency conditions dictated by thermal quenching.

The schematic presentation of thermal quenching efficiency given by Eq. (1) is shown in Fig. 3, the curve in this figure, gives the dependence of the thermal quenching efficiency on the activation temperature, from this simulated result we can see that the sensitivity increases with the activation temperature, reaching a maximum at 350 K and reducing significantly at 550 K. This behavior can be described by the thermal quenching effect.

6. Heating rate effect

Another important result of the model is that it reproduces the well-known decrease in the thermoluminescence (TL) signal due to thermal quenching. Specifically when TL glow curves are measured using a variable heating rate from 1 to 20 K/s, the TL intensity is found to decrease as the heating rate increases. The result of simulating the TL glow curves using different heating rates is shown in Fig. 4, using typical kinetic parameters for the 598 K TL peak of quartz (activation energy and frequency factor). As the heating rate increases, the TL glow peaks become wider and shift toward higher temperatures, while their intensity decreases significantly.

Thus at low heating rates the TL peak may appear in a range where thermal quenching is minimal, whereas at high heating rates the peak temperature may be such that thermal quenching is strong (Nanjundaswamy et al., 2002). Berkane-Krachi et al. (2002) studied the heating rate effect on TL response and showed that the TL response decreases when heating rate increases and this reduction in TL sensitivity is well described using a Mott–Seitz theory (Akselrod et al., 1998). Thermal quenching causes a shift of the temperature of maximum intensity T_m of a TL glow-peak toward lower temperatures (Akselrod et al., 1998). So the T_m of the quenched glow-peak is shifted to higher temperatures as a function of the heating rate. The shift of the temperature maximum of the thermoluminescence glow curves is represented in Fig. 5.

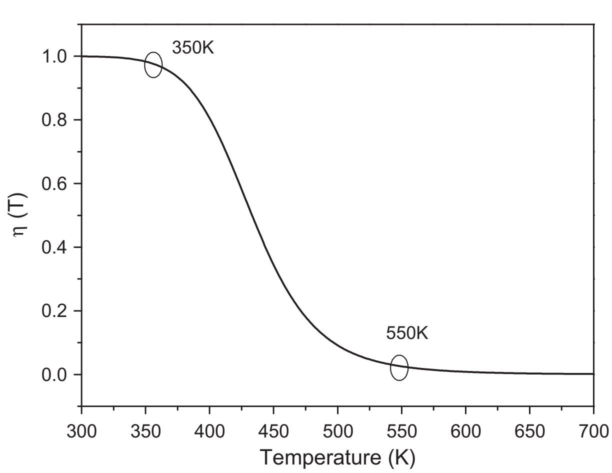

Figure 3 The thermal quenching efficiency of quartz.

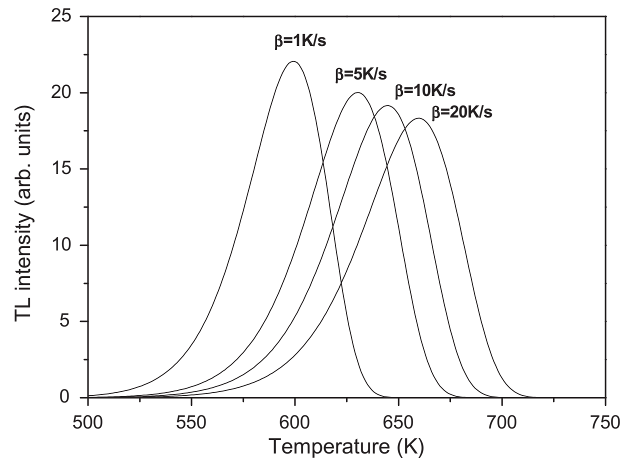

Figure 4 Effect of the heating rate β on the shape and the position of the 598 K glow peak. The TL intensity is plotted as a function of temperature. Parameter values are the same as Fig. 2.

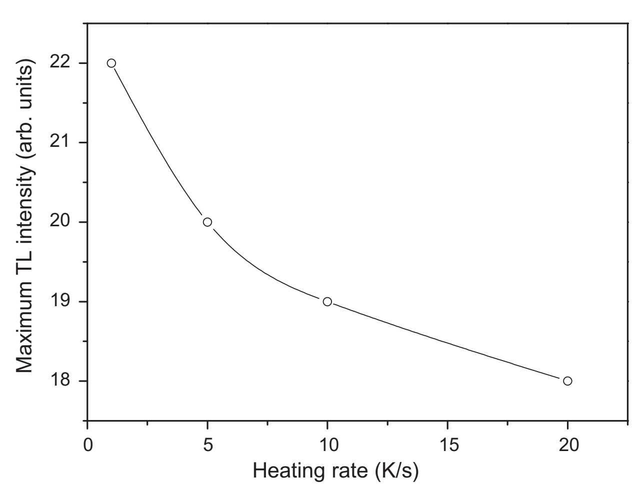

Figure 5 The behavior of the peak maximum intensity I_m, of glow-peak represented in Fig. 4 as a function of heating rate.

7. Conclusion

In the present paper, we propose a simple energy-band model which may explain the thermal quenching effect for the 325 °C glow peak of thermoluminescence of quartz studied previously by Wintle (1975). The investigation present here is based on the two-stage thermal stimulation of thermoluminescence model (Chen et al., 2012). Our model can be applied to several types of luminescence experiments and provides a satisfactory description of the thermal quenching kinetics in the case of TL experiments. An important result of the model is that it reproduces the thermoluminescence (TL) peak of quartz (325 °C peak). Another important result of this study showed that the peak temperatures of all peaks shift to high temperatures and the maximum TL intensity of peaks decreases as the heating rate increases as expected in theory. In the future and using the present model, we can explain the thermal quenching effect in many thermoluminescent materials.

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